Elemental analysis of rain- and fresh water by neutron activation analysis

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Abstract Analysis of rain-and fresh water for trace constituents is a mandatory part of environmental monitoring. This text gives a survey of neutron activation analysis (NAA) within the framework of current environmental water research programmes, based on the practice developed in co-operation with the Dutch Energy Research Centre at Petten (ECN). While the procedures reported in literature cover about thirty five elements, our routine procedures of instrumental neutron activation analysis (INAA) is limited to ten to fifteen elements. The use of some dedicated radiochemical separations (RNAA) adds another six, some of which are speciated as well. Current contributions of NAA to water analysis center on determination and speciation of anionic trace elements, notably Br, I, As, and Se, on the assay of some ultra traces like Ag, Au and Hg and on validation.

Keywords INAA, RNAA, Elemental and speciation analysis of water

CLC numbers X131.2, X830.2, O657.4

1 GENERAL

In environmental water monitoring radioanalysis supplies concentrations, net transport and-exchange rates. The kinetic determinations are based on radiotracer experiments mostly, either in the laboratory or under well defined field conditions. The main use of element[1] or species[2,3] determination by neutron activation analysis is closely related to field work. The link often consists of some preconcentration step. Characterization by multi-element determinations and measurement of transport rates by way of stable tracers[4] are additional applications.

Radioanalysis of water usually makes part of analytical programmes in which it is mandatory to combine *in situ* measurements and laboratory determinations. At the spot, on board a ship or an aeroplane, samples are taken and preconditioned for transport to the (radio-)chemical laboratory. The data obtained should fit into the pattern set by the continuous measurements of salinity, Eh(oxydation potential), pH, BOD(biological oxygen demand), concentrations of major anions, concentration of particulate matter and the accompanying particle spectrum.

Relations between these two groups of results may sometimes be found by radiotracer experiments in confined but sufficiently large volumes. Distribution coefficients,

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Manuscript received date: 2000-11-27

kinetics of exchange at equilibrium and the response to step- or gradient-like changes have to be considered in such investigations. Similar information can be obtained from the measurement of "natural" radioactivity which reflects, especially in its desequilibria, the influence of continuous mass transport between the aqueous and solid phases.

Next to the addition to other analytical methods, radioanalysis is applied for validation of their results.

From a practical point of view, it is convenient to distinguish between the applications to rain-, fresh-, ground- and seawater. Here only the first two are considered.

In the case of rainwater[5,7~10] and snow[5,6,11] the obvious use of NAA is the determination of trace elements. The main reasons are characterization and pollution studies, partly as an extension of "fingerprinting" by stable isotopes. Radiotracer experiments are virtually impossible; stable tracers can be used sporadically. With fresh water the emphasis is again on NAA for trace determination, mainly of anions, and experiments with stable tracers[12~14].

2 INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

2.1 Survey of literature

The application of INAA to water is limited by interfering radionuclides from Na, K and Br; consequently its use is mostly on relatively pure water, first of all on rainwater. A further restriction is caused by gammalysis, resulting in pressure build-up. One finds

Matrix	Elements determined (and maximal thermal neutron flux used)
Snow	Na, K, Mn, Ni[11,15]
Rainwater	Cl, La, K, Na, Co, In, Fe, Sc, Mn, Cs, Br, Ag, Sb, Cd, Cr, Hg, Ce, Sm[10] ($\phi_{th}=10^{12}$ cm^{-2}·s^{-1})
	Na, Al, Cl, V, Cr, Fe, Mn, Co, Cu, Zn, Br, In, Sb, I, U[16] ($\phi_{th}=5\times10^{13}$ cm^{-2}·s^{-1})
	Al, Ba, Cl, Co, I, Mg, Mn, Na, Sb, Ti, Zn[7] ($\phi_{th}=10^{12}$cm^{-2}·s^{-1})
	Ag, Al, As, Au, Ba, Br, Ca, Ce, Cl, Co, Cr, Cu, Dy, Fe, Hf, Hg, I, K, La, Mg,Mn Na, Rb, Sb, Sc, Se, Sm, Sr, Ti, V, Zn[8] ($\phi_{th}=5\times10^{11}$cm^{-2}·s^{-1})
Surface water	Br, Cs, Ca, La, Rb, Fe, Co[12] ($\phi_{th}= 10^{14}$cm^{-2}·s^{-1})
	Na, Rb, Cs, Ca, Ba, Sb, Br, Sc, La, Ce,Sm, Eu, Yb, Th, U, Cr, Fe, Co, Zn, Au, Cd Hg[17,18]
	Na, Sc, Ca, Cr, Fe, Ni, Co, Zn, As, Se, Br, Rb, Ag, Sb, Te, Cs, Ba, La, Eu, Tb, Yb, Hf, Ta, Au, Hg, Th, U[13]
	As, Ba, Br, Ca, Cd, Co, Cr, Cu, Eu, Fe, Hg, K, La, Mn, Mo, Na, Sb, Sc, .Sr, U W, Zn[14] ($\phi_{th}=2\times10^{13}$cm^{-2}·s^{-1})

The quality of these determinations varies with the element involved.

In Ref.[17] the precision of the determination is worse than 20% for 4 elements (Ce, Eu, Hf, Yb), 10-20% for 16 elements (Ag, As, Au, Ba, Ca, Co, Cr, Fe, Hg, I, La, Rb, Sb, Sm, Sr, Th) and better than 10% for 11 elements (Al, Br, Cl, Cs, K, Mg, Mn, Na, Sc, V, Zn). The main limiting factor is counting statistics.

Usually the samples are filtered through nuclepore[8,9] or millipore[14,19] filters.

Preconcentration may be omitted[16,17] or consists of evaporation by heating[10,11,13] or freeze-drying[7,13]. Concentration-factors are in the order of 10^2-10^3.

The main advantage of INAA and RNAA over other analytical methods is their relative insensitivity towards contamination. If aliquots are stored in precleaned plastic containers and kept frozen during transport, interference from the capsule is negligible. Plastic bags made by heatsealing polythene foil are used for large samples[9].

Irradiation is done in plastic vials whenever possible[7,9,11]. For fluxes over $\sim10^{13}\mathrm{cm}^{-2}\cdot\mathrm{s}^{-1}$, quartz is applied[16].

Irradiation usually implies two different activations on separate aliquots: Short activation during 1~10 minutes, followed by 2~10 minutes decay and 2~5 minutes counting. Long irradiation for 3~40 h with 1~14 days cooling and measurement during 1 to 5 hours. Occasionally high-flux irradiations ($\phi_{\mathrm{th}}\sim10^{14}\,\mathrm{cm}^{-2}\cdot\mathrm{s}^{-1}$) are applied on solid residues. Activation takes a few days, cooling 2~4 weeks and measurement 30 minutes to a few hours.

Standards are based on an inert support, like active carbon, loaded with known amounts of spectrometrically compatible elements.

2.2 Standard elemental analysis

The procedure used in the radiochemical laboratory of ECN comprises about 14 trace elements[16]. It is based on irradiation in two pneumatic rabbit systems, a "slow" (PRS) and a "fast" one (FASY), both with $\sim 5\times10^{13}\,\mathrm{cm}^{-2}\cdot\mathrm{s}^{-1}$ and on a 'high flux' facility (PIF), with $5\sim8\times10^{13}\mathrm{cm}^{-2}\cdot\mathrm{s}^{-1}$ thermal flux. A modular system of polythene capsules with snap caps is used in the rabbit systems, while high purity quartz is applied in the PIF.

2.2.1 Sampling and sample treatment

Rain is collected at 150 cm above the ground in a wet only sampler. A black bag surrounds the vessel to inhibit the growth of algae during the storage. If iron has to be determined, some dilute double distilled nitric acid is placed in the vessel prior to sampling to prevent adsorption to the container wall. As soon as possible after the sampling, the samples are filtered. The contamination during the filtration by the filter and filtration apparatus must be minimized.

2.2.2 Irradiation and processing of aliquots

Determination of V is based on 2 min irradiation in the FASY; that of Na,Al,Cl,Mn and Br on 4 min in the PRS. Irradiations on preconcentrates are performed in the PIF for the assay of Cr, Fe, Co, Zn and Sb. Analytical procedures are:

(a) Slow rabbit system (PRS)

Aliquots of 2.5 mL rain water are introduced into clean capsules by pipetting.

-Irradiation takes 4 minutes in a thermal neutron flux of $5\times10^{13}\,\mathrm{cm}^{-2}.\mathrm{s}^{-1}$.

-Samples return to the chemical laboratory in 3 minutes. The dose rate at contact on a sample capsule is then ~1 mSv.h^{-1}.

-Capsules are opened and two ml amounts are pipetted in polythene counting vials.

-Counting with a Ge-detector connected to a 2048 channel analyzer starts 4~5 minutes after the end of the irradiation. The usual counting time is 10 minutes. The data output is transmitted to a minicomputer and processed.

- Standards are processed identically.

(b) Fast rabbit system (FASY)

-Aliquots of 0.8 mL rain water are introduced into clean capsules by pipetting.

-The samples are irradiated during 2 minutes in a thermal neutron flux of 3×10^{13} cm^{-2}·s^{-1}. The irradiated sample automatically arrives in the counting position in front of a 45 cm^3 coaxial Ge detector in a lead shielding. The average distance sample-detector surface is 5 mm. The Ge detector is connected to a 400 channel analyzer.

-Counting in the life-time mode is started manually as soon as the total dead-time is lower than 30%. Usually this takes 2 minutes. Preset counting time is normally 2 minutes.

-The area under the 1434 keV photopeak of ^{52}V is determined. Corrections for the decay during measurement are applied[20,21].

(c) 'High flux' facility (PIF)

-Hundred mL of rain water is preconcentrated in two steps. First the volume is reduced to ~10 mL by evaporation of the rain water sample during 6 hours on a water bath of 75°C under a continuous flow of air filtered through a membrane filter of 0.45μm. The residue is weighted and the greatest part transferred to a clean quartz capsule. The yield of this transfer is determined by weighing. The sample is taken to dryness by heating the quartz ampoule on a hot plate under a gentle stream of filtered air.

-The capsule and an iron fluxmonitor, placed under the bottom of the ampoule, are wrapped in a thin aluminium sheet.

-The sample capsule is transferred to an aluminium capsule which is closed by welding. Irradiation takes 2 days at a thermal neutron flux of $\sim 5 \times 10^{13}$cm^{-2}·s^{-1}.

-Samples are allowed to cool for 3 weeks. The contents of the capsules are transferred to polythene counting vials by at least three subsequent washings with 0.8 M HCl containing carrier amounts of the elements of interest. The concentration of the carriers used is ~10 mg·L^{-1}.

-Counting is performed with a 45 cm^3 Ge detector connected to a 4096 channel analyzer. Usual counting time is 50 minutes.

2.2.3. Results

(a) PRS (Pneumatic Rabbit System)

The observed gamma energies are due to the following short-lived radionuclides ^{24}Na, ^{28}Al, ^{38}Cl, ^{41}Ar, ^{52}V, ^{56}Mn, ^{66}Cu, ^{80}Br and ^{128}I. The obtained specific count rates of the different nuclides can be used for the calculation of the limits of determination following Currie[22]. Results are given in Table 1. They compare favourably with those obtained by AAS (atomic absorption spectrometry). Instrumental neutron activation analysis of bromine based on ^{80}Br ($T_{1/2}$=17.6 min, E_γ=617 keV) can lead to erroneous results if one is not aware of the spectral interference from the double escape peak of ^{38}Cl ($T_{1/2}$=37.3 min); E_γ=620 keV. As the ratio of bromine to chlorine in rain water is of the order of 0.01, this contribution by ^{38}Cl to the ^{80}Br peak area can be considerable. A correction can be made if the ratio of the peak areas of E_γ and that at 1642 keV is known. This ratio is around 0.028.

Table 1 The specific count rate and limit of determination of some short-lived radionuclides for INAA of rain water[16]

Element	Radio-nuclide	$T_{1/2}$	Gamma ray measured/keV	Specific count rate * /counts·min^{-1} · μg^{-1}	Limit of determination (1/k_Q=0.1[12])		
					μ_B/counts	L_Q/ng	L_Q/μg·L^{-1}
Sodium	^{24}Na	15 h	1368	2.2×10^3	1300	19	9.5
Aluminium	^{28}Al	2.3 min	1779	1.3×10^5	2900	6	3
Chlorine	^{38}Cl	37.3 min	1642	2.1×10^3	1900	28	14
Vanadium	^{52}V	3.75 min	1434	5.8×10^5	200	0.2	0.1
Manganese	^{56}Mn	2.6 h	847	1.6×10^5	1900	0.3	0.15
Cobalt	^{60m}Co	10.5 min	58.5	1.4×10^5	4500	0.9	0.45
Copper	^{66}Cu	5.1 min	1039	1.4×10^4	2600	14	7
Bromine	^{80}Br	17.6 min	617	2.3×10^4	3700	4.1	2.05
Iodine	^{128}I	25.2 min	443	1.9×10^5	5400	0.5	0.25

*Data refer to the end of the irradiation: irradiation time 4 minutes in PRS-1

Experimental conditions: *Irradiation time 4 min* — μ_B=*Absolute limit in counts*
Cooling time 4.5 min — L_Q=Absolute limit in ng or
Counting time 10 min — relative (limit) in μg·L^{-1}
Rain water aliquot volume 2 mL — $k_Q\simeq10$

(b) Fast rabbit System

The measurement of short-lived radionuclides in rain water by a fast rabbit system has some disadvantages. First, the sample capsule cannot be removed. Then the specific count rates will be lower due to the shorter irradiation time. Finally the aliquot volume is small (0.8 mL). The half-life is decisive. The determination of vanadium in large series of rain water samples is a good example[20]. Table 2 gives the reproducibility obtained with Dutch rain water.

Table 2 The reproducibility of instrumental neutron activation analysis of rain water for short-lived radionuclides[16]

Element	Average concentration	Standard deviation	
		absolute	relative/%
Na	1.51 mg·L^{-1}	0.08 mg·L^{-1}	5.3
Al	63.4 μg·L^{-1}	8.2 μg·L^{-1}	12.9
Cl	2.65 mg·L^{-1}	0.06 mg·L^{-1}	2.3
V	3.11 μg·L^{-1}	0.14 μg·L^{-1}	4.5
Mn	17.7 μg·L^{-1}	0.6 μg·L^{-1}	3.4
Co	0.44 μg·L^{-1}	0.15 μg·L^{-1}	34
Cu	8.0 μg·L^{-1}	3.4 μg·L^{-1}	43
Br	22.8 μg·L^{-1}	1.4 μg·L^{-1}	6.1
I	0.47 μg·L^{-1}	0.11 μg·L^{-1}	23

(c) Poolside isotope facility

Radiotracer experiments showed that the losses of Cr, Fe, Co, Zn and Sb from rain water during preconcentration by evaporation to dryness are negligible. After 2 days in the PIF and a cooling period of a few weeks the main peaks observed belong to ^{40}K, ^{51}Cr, ^{59}Fe, ^{60}Co, ^{65}Zn and ^{124}Sb. The obtained specific count rates and the limits of determination of the elements of interest are given in Table 3 while the reproducibility is summarized in Table 4.

Table 3 The specific count rate and limit of determination of some long-lived radionuclides for INAA of rain water[16]

Element	Radio-nuclide	$T_{1/2}$	Gamma ray measured/keV	Specific count rate* /counts·min^{-1}·μg^{-1}	Limit of determination ($1/k_Q=0.1$[22])		
					μ_B/counts	L_Q/ng	L_Q/μg·L^{-1}
Chromium	^{51}Cr	27.8 d	320	5.7×10^5	1600	1.6	0.0016
Iron	^{59}Fe	45 d	1099	3.3×10^3	400	130	1.3
Cobalt	^{60}Co	5.26 y	1173	1.3×10^6	450	0.25	0.0025
Zinc	^{65}Zn	245 d	1115	5.0×10^4	400	6.5	0.065
Antimony	^{124}Sb	60.3 d	602	6.2×10^5	800	0.8	0.008

*Data refer to the end of the irradiation: irradiation time 2 days in PIF

Experimental conditions: Irradiation time 2 days; μ_B=Absolute limit in counts
Cooling time 3 weeks; L_Q=Absolute limit in ng or
Counting time 50 minutes relative in μg·L^{-1}
Rain water aliquot volume 100 mL $k_Q\simeq10$

Table 4 The reproducibility of instrumental neutron activation analysis of rain water for long-lived radionuclides

Element	Average concentration /μg·L^{-1}	Standard deviation	
		Absolute/μg·L^{-1}	Relative/%
Cr	0.36	0.02	5.6
Fe	12.7	0.9	7.0
Co	0.47	0.02	4.9
Zn	71	6	8.5
Sb	3.51	0.14	4.0

3 DEDICATED RNAA OF RAIN WATER

Next to INAA, the routine programme consists of some RNAA procedures. They provide extra elements or higher sensitivity.

3.1. Bromine and iodine by isotopic exchange[23]

Radionuclides are isolated by isotopic exchange between the irradiated sample and a solution of Br_2 or I_2 in CCl_4. The method does not give information on the chemical species. The lower limits of determination are 1 μg Br·L^{-1} and 0.1μg I·L^{-1}.

The procedure consists of the following steps :

-Irradiation of a 2.5 mL aliquot at $\sim5\times10^{13}$ cm^{-2}·s^{-1} during <5 minutes.

-*Isotopic exchange between the sample and a solution of* Br_2 *or* I_2 *in* CCl_4.

-Measurement with a NaI or Ge detector.

Isotopic exchange has been used for the isolation of ^{131}I from fission products[24]. The method is fast and simple. The chemical yield depends on the amount of Br_2 or I_2 in the organic phase and, in principle, on the chemical form of the halogens. Whereas exchange between X_2 and X' or XO' (X=halogen) is very fast[25], that between X_2 and XO'_3 is slow and strongly pH-dependent[26]. The time required for 50% exchange between X_2 and the corresponding organohalogen compounds varies from a few minutes to many hours[27]. However, for the analytical procedure this is of small importance as the activated halogen atoms are set free by recoil[28,29]. Their subsequent transformation into exchanging species is governed by the bulk composition of the solution[29] and the gamma dose. The exchange yield, as measured with tracers, tends to become constant at concentrations above 10 mg Br_2 or I_2 per mL CCl_4; the value is (88±2)% for bromine and (89±2)% for iodine. To obtain the latter yield, it is mandatory to adjust the pH to 11 with ammonia prior to the irradiation.

3.1.1 Sensitivity of the method

After 4 minutes irradiation in a thermal neutron flux of $5\times10^{13}\,cm^{-2}\cdot s^{-1}$ and a decay time of 9 minutes the specific count rates are:

$3'' \times 3''$ NaI well type crystal 3×10^5 counts $min^{-1}\,\mu g^{-1}$; 45 cm^3 coaxial Ge detector 1.6×10^4 counts $min^{-1}\cdot\mu g^{-1}$ (sample directly on top of the detector). With a sample volume of 2 mL (effective volume =1.6 mL) and an exchange yield of ~90%, the lower limit of the determination is $1.0\mu g\cdot L^{-1}$ for bromine and $0.1\,\mu g\cdot L^{-1}$ for iodide (based on a minimal detectable count rate of 25 $counts\cdot min^{-1}$).

3.1.2 Results

Large samples of tap water, rain water and surface water were analyzed five times to check the reproducibility:

	Br-concentration/$\mu g\cdot L^{-1}$	I-concentration/$\mu g\cdot L^{-1}$
Rain water	12.87±0.95	0.73±0.07
Tap water	230±10	4.14±0.34
Surface water	309±31	2.46± 0.36

3.2 Iodate by anion exchange and subsequent INAA[30,31]

A separation of I' and IO'_3 prior to the irradiation is possible by stepwise elution from a Dowex-2 × 8 mm^2 (OH′) column, using 0.1 mol/L NaOH or 0.1 mol/L NH_4OH as the eluent. Due to the interference by ^{24}Na, $T_{1/2}=15\,h$, it is preferable to use NH_4OH. As the affinity of Cl' and NO'_3 is larger than that of IO'_3, concentrations of these interferences should be kept below ~25 $mg\cdot mL^{-1}$ and ~10 $mg\cdot mL^{-1}$ respectively.

3.2.1 Analytical procedure[30]

In the laboratory of ECN, the following procedure was chosen as a result of tracer experiments. Columns of ~0.4 g resin are prepared and connected to tygon tubes (cf. Fig.1). A rain water sample is filtered through a 0.45μm membrane filter. A volume of 20~25 mL is then fed into the column at a flow rate of 0.22 $mL\cdot min^{-1}$, controlled by a peristaltic pump. Columns are washed with 3 mL double distilled water and transferred to cleaned elution systems. They are eluted with 0.1 mol/L NH_4OH which is added dropwise at a flow rate of 0.3 $mL\cdot min^{-1}$. Volumes of ~10 mL are collected in the irradiation capsules. These are sealed and cooled in liquid nitrogen. Irradiation is carried out for 4 min at a thermal neutron flux of $5\times10^{13}\,cm^{-2}\cdot s^{-1}$. Cooling time is ~15 min. Aliquots of 8 mL are pipetted into polythene extraction vials in which 200μL concentrated HCl is present and are shaken with 5 mL of a I_2 solution in CCl_4 (6 mg $I_2\cdot mL^{-1}$) for at least 1 min. Aliquots of 4 mL are taken from the organic phase and transferred to test tubes and counted for 15 min. with a NaI well type detector connected to a 400 channel analyzer. The area under the 442 keV photopeak of ^{128}I ($T_{1/2}$=25.2 min) is evaluated. Iodate solutions (50μg $I\cdot L^{-1}$) in double distilled water are used as standards.

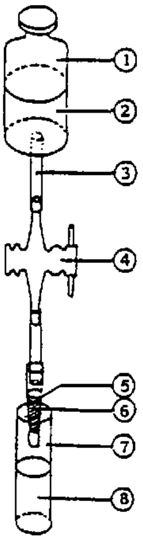

Fig.1 The elution system for the I'- IO_3' separation and for the determination of IO_3', after Ref.[30]

1. polythene bottle (V=100 mL), 2. eleuent (0.1 mol/L NH_4OH), 3. polythene tube (4 mm i.d), 4. tap (teflon), 5. glasswool, 6. Dowex-2×8(OH), 7. irradiation capsule, 8. the eluate

3.2.2 Results

The relative standard deviation, observed for standard solutions varies from 21% at 50ppb till ~20% at 0.2 ppb. Concentrations in Dutch rain water are of the order of 2 $\mu g I'\cdot L^{-1}$ and 1μg $IO_3'\cdot L^{-1}$.

3.3 Arsenic[32]

Coprecipitation of As(III) with dibenzyldithiocarbamate (DBDTC) is followed by reduction of As(V) with thiosulphate and a second coprecipitation. The solids are collected on microfilters and submitted to NAA. The procedure is shown in Fig.2

3.4 Selenium[33]

The determination of selenium is analogous to that of arsenic. A difference is met in the addition of 100 mg phenolphtalein to ensure the stability of the precipitate. Irradiation and counting time are adjusted to the radionuclide, ^{75}Se, $T_{1/2}$=120d. The limits of determination and detection are equal to those for arsenic.

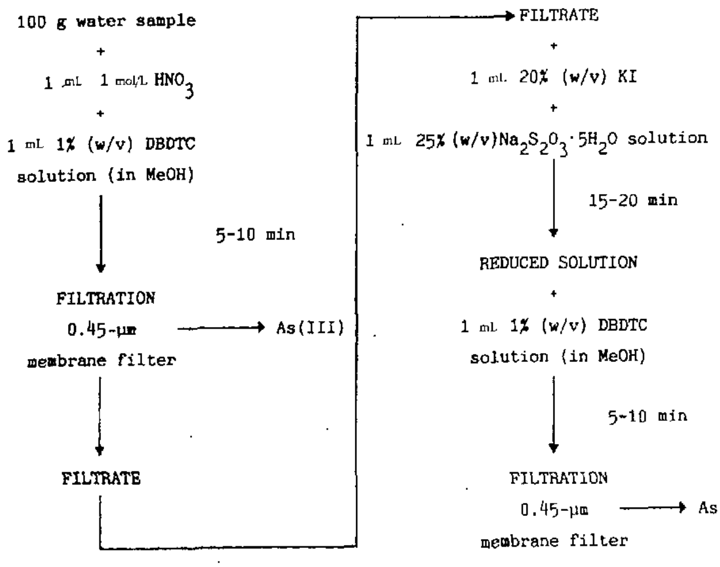

Fig.2 The optimized procedure for 100 mL samples runs as shown above. Loaded filters are dried over silicagel and packed in $18\times9\,\mathrm{mm}^2$ polythene containers equipped with iron flux monitors.

Irradiation at a flux of $5\times10^{13}\mathrm{cm}^{-2}\mathrm{s}^{-1}$ during 15 minutes and cooling for day is followed by counting with a $45\,\mathrm{cm}^3$ Ge-detector for the 559 keV peak of ^{86}As, $T_{1/2}=26.4$ h. The lower limit of determination is $\sim0.05\,\mu\mathrm{g\cdot L^{-1}}$, that of detection $\sim1\,\mathrm{ng\cdot L^{-1}}$.

3.5 Silver by cation-exchange and subsequent NAA[34]

Rain, melted hail or snow is made pH=3 with acetic acid and dripped through a small column of a cation exchange resin at a low flow rate. The Ag^{+}-ions are then eluted with 0.1 mol/L NH_4CNS; about 25 mL is necessary. The collection efficiency is (96±2), that of the elution (80±7)% in the first 5 mL of the eluate for amounts from 10^{-10} to 10^{-8} g silver. Blank eluent aliquots are processed identically. The determination is based on the reaction $^{109}\mathrm{Ag}(\mathrm{n},\gamma)\,^{110}\mathrm{Ag}$, $T_{1/2}=24$ s.

Procedure

-Ion-exchange on a $0.7\times2\,\mathrm{cm}^2$ column of 0.5 g Dowex-50, 200 mesh at a flow rate of $\leq5\,\mathrm{mL\cdot min^{-1}}$.

-Elimination of remaining fluid on top of the column. Addition of 5 mL 0.1 mol/L NH_4CNS and equilibration for 5 minutes.

-The eluate is siphoned off, sealed in a polythene film and transferred to an irradiation vial. Irradiation takes 40-60 seconds at a thermal neutron flux of $4\times10^{12}\,\mathrm{cm}^{-2}\mathrm{s}^{-1}$.

-Counting with a 3"×3" NaI well-type crystal starts ~20 seconds after the end of the irradiation to eliminate most of the ^{16}N, $T_{1/2}=7.3$ s, activity produced by $^{16}\mathrm{O}\,(\mathrm{n,p})^{16}\mathrm{N}$.

Silver concentrations in snow water vary from 5 to 50 ng·L^{-1}.

3.6 Mercury[35]

Inorganic, organic and particulate mercury are determined in large samples as shown below. The total amount of mercury is collected by passing a known volume of the crude sample through an activated carbon column (A). Part of the sample is centrifuged and a known fraction of the clear liquid is led through an activated carbon column (B-1). This yields the inorganic dissolved mercury. Another centrifuged fraction is transferred to an aeration vessel and the mercury is reduced with stannous chloride and led through an active carbon adsorber.

The carbon fractions and the isolated suspended matter are analysed by NAA using ^{197m}Hg, $T_{1/2}$=66h, E=77 keV. Organic mercury is obtained as the difference between B-1 and B-2. The analytical procedure is summarized in Fig.3.

The limits of determination and detection are 10 and 1 ng·L^{-1} respectively.

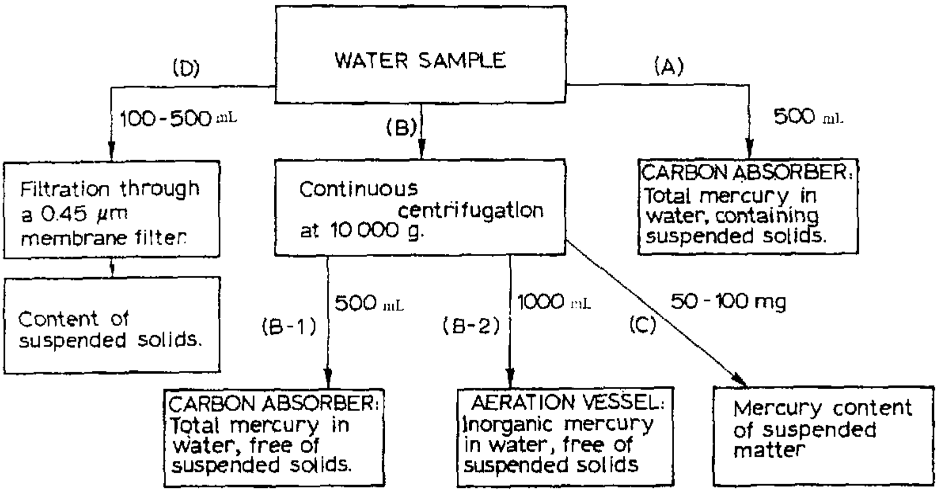

Fig.3 Mercury analysis procedure

4 CONCLUSIONS

-Routine INAA of rainwater yields up to 14 element concentrations, depending on the applied neutron flux. Dedicated RNAA adds a few more; its most important contribution is the speciation of iodine.

-The wider scope of literature reports on rainwater analysis reflects the maximal rather than the usual result.

-An independent application of NAA is met in the mapping of the distribution of stable tracers added to the exhaust of an industrial plant.

References

1 Gabarino J R *et al.* Anal Chem, 1985, **57**:46R

2 Florence T M, Batley G E. CRC critical reviews in analytical chemistry 1980, 219

3 Florence T M. Talanta, 1982, **29**:345

4 Knaus R M. Env Sci Technol, 1981, **15**:809

5 Landsberger S *et al.* Trace analysis. New York: Academic Press, 1985, 237, and Int J Environ Anal Chem, 1984, **16**:95

6 Murozumi M *et al.* Geochim Cosmochim Acta, 1969, **33**:1247

7 Ndiokwere C L. Radioisotopes, 1982, **31**:583

8 Hamilton E P, Chatt A. J Radioanal Chem, 1982, **71**:29

9 Schutijser P *et al.* Anal Chim Acta, 1978, **100**:75

10 Bogen J. Atmosph Environ, 1974, **8**:835

11 Hanappe F *et al.* Earth Planet Sci, 1968, **4**:487

12 Schmitz J *et al.* Report KfK-1533 Karlsruhe FRG, 1972

13 Motamedi K. Report GKSS-76/E/38 Geesthacht FRG, 1976

14 Bart G, Gunten H R von. Int J Environ Anal Chem, 1979, **6**:25

15 Brocas J, Piciotto E. J Geophys Res, 1967, **72**:2229

16 Luten J B. Neutron activation analysis of trace elements in rainwater. Thesis Utrecht University and Report ECN-20, Petten, The Netherlands, 1977

17 Salbu B *et al.* Anal Chem, 1975, **47**:1011

18 Jorstad K *et al.* Chem Geol, 1982, **36**:325

19 Cawse P A, Peirson D H. Report AERE-R 7134 Harwell, UK, 1972

20 Das H A *et al.* Radioanal Radiochem Lett, 1975, **21**:61

21 Woittiez J R W *et al.* J Radioanal Chem, 1979, **53**:111

22 Currie L A. Anal Chem, 1968, **40**:586

23 Luten J B. J Radioanal Chem, 1977, **35**:147

24 Palagyi S *et al.* Radiochem Radioanal Lett, 1974, **20**:101, 111

25 Haissinky M. J Chim Phys, 1950, **47**:957

26 Myers D E *et al.* J Am Chem Soc, 1950, **72**:897

27 Brodsky A E. Isotopenchemie Akademieverlag Berlin DDR, 1961, 380

28 Gordus A A, Hsiung Ch. J Chem Phys, 1962, **36**:954

29 Malvano R, Grosso P. J Nucl Biol Med, 1968, **12**:86

30 Luten J B *et al.* J Radioanal Chem, 1978, **43**:175

31 Takiura K, Takino Y. Japan Analyst, 1961, **10**:483

32 van Elteren J T *et al.* Anal Chim Acta, 1989, **222**:159

33 Saleh A L *et al.* J Radioanal Nucl Chem, 1990, **140**:357

34 Warburton J A, Young L G. Anal Chem, 1972, **44**:2043

35 van der Sloot H A, Das H A. Anal Chim Acta, 1974, **73**:235